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POTENTIAL STRUCTURAL MATERIAL PROBLEMS IN A
HYDROGEN ENERGY SYSTEM

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SUMMARY

Potential structural material problems that may be encountered in the three components of a hydrogen energy system - production, transmission/storage, and utilization - have been identified. Hydrogen embrittlement, corrosion, oxidation, and erosion may occur during the production of hydrogen. Hydrogen embrittlement is of major concern during both transmission and utilization of hydrogen. Specific materials research and development programs necessary to support a hydrogen energy system are described. An awareness of probable shortages of strategic materials has been maintained in these suggested programs.

INTRODUCTION

The Hydrogen Energy Systems Technology (HEST) Study was a NASA funded effort to determine national needs for research and technology in hydrogen production, handling and use. The Jet Propulsion Laboratory was assigned to conduct the study, supported by most NASA centers and several people within ERDA. The final report of the HEST Study was scheduled for submission to the NASA Office of Energy Programs in June 1975. In support of the HEST Study a materials working group was formed and was comprised of the authors of this report under the leadership of the senior author. This report constitutes most of the materials working group submission to the HEST Study

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The purpose of this report is to identify potential structural material problems that may be encountered within the three components of a hydrogen energy system - production, transmission/storage, and utilization (refs. 1 to 8). Although nonmetallic material problems are not covered in this report, we recognize that high pressure, high temperature seals may need development and that specialized problems such as compressor bearings, lubricants, insulation materials, etc. exist and must be solved for each design.

Many of the current and proposed hydrogen production processes involve chemical or thermochemical reactions that occur at elevated temperatures and pressures in a variety of aggressive environments. Continued exposure to such conditions may severely degrade the design mechanical properties of structural alloys, and so influence system reliability and increase maintenance costs. Since the specific operating conditions of many proposed hydrogen production processes have not yet been defined, the initial part of this report deals with material compatibility problems in a general way. The problems that are discussed are: hydrogen embrittlement, corrosion, oxidation, and erosion (see table I).

However, regardless of which hydrogen production processes eventually prove economically feasible, transmission and storage of hydrogen will always be required in a hydrogen energy system to link hydrogen production with utilization. Since such operational conditions are reasonably predictable, potential problems of hydrogen embrittlement are considered in detail in the main part of this report. The various types of hydrogen embrittlement and their occurrence in hydrogen energy systems are identified.

Specific materials research and development programs necessary to support the evolution of a hydrogen energy system are identified. An awareness of future probable shortages in strategic materials is maintained in arriving at these research and development recommendations.

GENERAL STRUCTURAL MATERIAL PROBLEMS

Interfacing with Process Heat Sources

Nuclear heat source. - Waste heat or steam generated in boiling or pressurized water reactors is of limited value as process heat for thermochemical water splitting reactions for all feed stocks because the temperature is only a few hundred degrees Celsius. With current commercial designs of high temperature gas cooled reactors (HTGR), helium temperatures of 750°C are achieved. With present fuel technology, reactor designs can achieve helium temperatures of 900°C . With advanced fuel technology, temperatures of 1000°C in the primary helium coolant

may be realized. Process heat temperatures reached in breeder and fusion reactors will be limited by liquid coolants and their containment materials.

The primary coolants considered for advanced reactor systems (refs. 9 to 12) include helium and carbon dioxide gases, liquid lithium and sodium, and fused salts. Depending on the type of reactor and the coolant used, there will be large induced radioactivity and/or small amounts of radioactive fission products in the coolant. The radioactive material may be either suspended solids, gases, or elements dissolved in liquid coolants. Of particular concern is tritium gas because it has a high permeation rate through many structural materials and it may also act as an embrittling agent. The permeation problem in fusion reactor technology is more severe than in other types of reactors; work is in progress at Argonne National Laboratory and other laboratories to measure permeation rates and to develop permeation barriers.

Because of the risk of materials failures in primary coolant systems, the coolant hardware will be contained within the reactor pressure vessel and a heat exchanger for removing process heat may be incorporated. Even with an integrated heat exchanger, there is some concern about tritium permeating into the secondary working fluid system. If it were possible to use the primary coolant directly for process heat instead of using a second working fluid, there would be substantial benefits in overall cost and efficiency.

Another problem area is the availability of materials with adequate high temperature strength and corrosion resistance for the temperatures now projected for advanced reactor systems. It may be necessary to develop new superalloys for these applications.

Solar heat source. - Solar energy as a source of process heat for thermochemical water splitting only has merit if a special collector system is designed to reach high temperatures (refs. 13 to 16). In one proposed design (ref. 13) of the central receiver type, a large array of mirrors reflects the solar energy into an insulated cavity at the top of a centrally located tower. The energy is absorbed in a heat transfer fluid such as Hitec.¹ For generation of electrical power an exit temperature of approximately 500° C is being considered, which is somewhat higher than the recommended maximum operating temperature (450° C) for Hitec exposed to air. The practical upper limit in this solar energy application will depend upon the rates of salt decomposition. Mild steels have been used successfully for containing Hitec, but stainless steels or other alloys will probably be utilized in the high temperature portions of the system.

¹Dupont trade name for a mixture of nitrate and nitrite salts.

If a similar solar collection system is coupled with a thermochemical hydrogen production process, higher exit temperatures will probably be desirable (600° to 1000° C). Gases, liquid metals or molten salts might be used as the heat transfer fluid. It is also conceivable that a slurry or solution containing one of the process reactants could be used as the heat transfer fluid. More work is needed to evaluate fluid characteristics and to qualify a structural material for containment. Preliminary studies at Sandia-Livermore indicate that high solar energy collection efficiency can be attained in this temperature range if the materials problems can be solved.

It has been demonstrated that much higher temperatures (approximately 3900° C) can be obtained in solar furnaces (ref. 17). They have been used for growing crystals of metals with high melting points and extracting moisture from rocks. It is conceivable that such solar furnaces could be used for direct thermal cracking of water, but the associated material problems are formidable.

Geothermal heat source. - In most of the geothermal processes in use or under development, the temperature obtainable in process steam or other fluids is 300° C or less. An example is the Lawrence Livermore Laboratory program in which hot brine solutions will be used for electrical power generation in the Imperial Valley in California. The corrosion problem in handling the hot brine is very serious; the success of the program depends more on the solution on this material corrosion problem than any other factor.

Coal. - There do not appear to be any advantages to using coal for process heat to produce hydrogen because it will probably be more economical to gasify coal to produce methane (synthetic natural gas).

Hydrogen Production

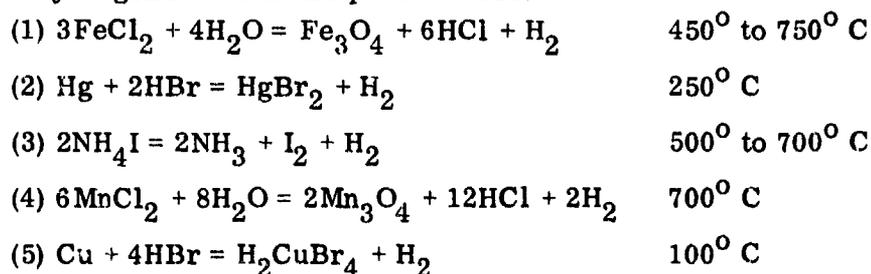
Thermochemical. - Many of the thermochemical cycles for splitting water that are being studied at various laboratories involve handling noxious reagents at high temperatures and high pressures, particularly salts, acids, and liquid metals. To the best of our knowledge, none of the laboratories in the United States investigating thermochemical cycles have supporting programs on containment materials. For the most part, the reactions are being studied in glass and platinum laboratory apparatus. MgO and vitreous carbon crucibles work well for selenides (ref. 18). At the Institute of Gas Technology, hot acid and salt solutions are contained in alumina and mullite without difficulty. At Sandia-Livermore, a glass ceramic has been used for hot HCl solutions. None of the programs in the U. S. have reached the stage where materials for scaling up a process have been selected.

The pioneering work on thermochemical cycles was done at the Euratom Joint Nuclear Research Laboratory at Ispra, Italy (ref. 19). During the past few years they have undertaken a rather extensive materials compatibility program to support their development work. Initial screening tests are done by exposing small specimens to corrosive media in quartz capsules. Some of the tests are conducted at high pressure by balancing the pressure built up in the capsules with an externally applied pressure. For candidate materials which exhibit good corrosion resistance in capsule tests, additional studies are made by pumping the corrosive media over the specimens in a recirculating test loop. In the future, metallic materials which have been proven to have good corrosion resistance will be subjected to stress corrosion tests.

The test program at Ispra is designed to evaluate materials under conditions which correspond exactly to thermochemical process conditions. For their Mark I cycle, suitable materials have been found for service in HgBr_2 , MgBr , and CaBr_2 . Depending on temperature, teflon, vitreous carbon, and high-nickel superalloys have attractive properties. Coatings are being investigated in an attempt to find cheaper materials. Compatibility of alloys with liquid Hg has been studied for space nuclear power systems (ref. 20), and the results should apply quite well to the Mark I and other mercury cycles. Cycles which use FeCl_2 and HCl are also receiving considerable attention in the materials program at Ispra.

Thus far, this discussion has been directed mainly to corrosion by hot acids and salt solutions. Another consideration is hydrogen compatibility of structural materials, which is not being investigated in any of the development programs and may not even be recognized as a potential problem at some laboratories.

Examples of some of the reactions under study at various laboratories in which hydrogen is one of the products are:



Note that in all of these reactions, hydrogen is present in combination with a halide. While our knowledge of materials behavior in pure hydrogen has progressed significantly in recent years the possible synergistic effect of hydrogen and a halide is an unexplored subject which deserves attention.

If one examines a list of the reactions under study (ref. 21) and the materials being used to contain them, it may seem that ceramic materials have more to

offer than metals and alloys for scaling up thermochemical processes. However, there are at least two reasons why metals and alloys should be used for at least part of the hardware. The first is that ceramic vessels and plumbing are difficult to fabricate. The other is that heat exchangers must be used if the processes are to be efficient, and only metals and alloys have thermal conductivities which are high enough for heat exchanger hardware.

Electrolysis. - The principal need in electrolysis technology is modernization of facilities to obtain higher efficiencies (refs. 22 and 23). At the same time, it is suggested that the cell operating temperature be increased from approximately 90° to 200° C. There would then be a need to replace asbestos separators, gasketing, and insulating materials. Improvements in electrode design could eliminate the need for new materials, particularly if a flow-through electrode were available. Relatively little research and development is in progress in these areas. Brookhaven National Laboratory is adapting Lurgi electrolyzers to produce hydrogen at a pressure of 32 atmospheres.

An area in which considerable progress has been made in the past few years is the development of solid electrolyte materials. The General Electric Co. has developed a solid polymer electrolyte which is being evaluated for hydrogen production. They are also investigating an electrochemical process for coupling the CO-CO₂ reaction to water splitting at a temperature of 800° C. Ceramic membranes with mixed ionic and electronic conductivity are being developed for this process. No containment materials work in support of this program has been started.

A few laboratories are studying hybrid thermochemical-electrochemical processes for hydrogen production. The key step is electrolysis of a halide or sulfate solution which will decompose at a lower voltage than in the electrolysis of pure water. Because of the aggressiveness of these chemical solutions, corrosion should be considered as a potential problem.

Coal gasification. - Many coal gasification processes require excess hydrogen for some reactions to maximize the methane yield. This hydrogen can be made by reacting steam with residual char. It is also possible to maximize hydrogen production during coal gasification by reacting all the carbon in coal in the water-shift chemical reaction. Potential material problems include erosion from coal particles, oxidation, and sulfidation at elevated temperatures (refs. 24 to 29).

Direct water splitting. - Other processes which should be mentioned briefly are thermal, photochemical, and radiolytic decomposition of water. Calculations and preliminary experiments have shown that these processes are probably not competitive with thermochemical cycles and electrolysis. The main reason is

that the rates and efficiencies of the processes are too low. Direct thermal decomposition would also require the use of expensive or perhaps strategic materials because thermal decomposition only occurs at very high temperatures.

Current processes. - Most of the hydrogen currently used in the United States is produced by steam reforming of natural gas. Steam reforming of naphtha or partial oxidation of residual oil are less frequently used production processes. These processes have been used for many years to produce hydrogen, and although associated material problems such as oxidation, erosion, and hydrogen embrittlement are generally under control, materials with longer lives would always be desirable.

HYDROGEN EMBRITTLEMENT OF STRUCTURAL ALLOYS

Types of Embrittlement

Potential hydrogen embrittlement problems exist in all three components of a hydrogen energy system - production, transmission/storage, and utilization.

Hydrogen embrittlement of metals is an old, a frequently encountered, and often misunderstood phenomenon. Metals processing, chemical, and petrochemical industries have experienced various types of material problems due to hydrogen for many years. More recently, however, the aerospace industry has experienced new and unexpected hydrogen embrittlement problems (ref. 30). Since there are many sources of hydrogen and several types of embrittlement, there are various theories for explaining the observed effects. Hydrogen embrittlement is classified into three types (ref. 31):

- (1) Hydrogen reaction embrittlement
- (2) Internal reversible hydrogen embrittlement
- (3) Hydrogen environment embrittlement

Hydrogen reaction embrittlement. - Although the source of hydrogen may be either atomic or molecular hydrogen, this type of embrittlement is quite distinct from the other two types. Once hydrogen is absorbed, it may react to form a new phase near the surface of the metal or diffuse substantial distances within the metal before it reacts. Hydrogen can react with itself, with the metal, or with a foreign element in the metal. The chemical reactions that comprise this type of embrittlement or attack are well known and are encountered frequently in the petrochemical industry. The new phases formed by these reactions are usually quite stable and embrittlement is not reversible during low temperature aging treatments.

Hydrogen can react with the metal or with an alloying element to form a hydride (MH_x). Hydride phase formation can be either spontaneous or strain induced.

Atomic hydrogen can react with itself within the metal to form molecular hydrogen (H_2). This problem is frequently encountered after steel processing and welding and has been termed flaking or "fish-eyes." Hydrogen can also react with a foreign element in the metal to form a gas. The so-called "hydrogen attack" (see fig. 1) is the reaction with carbon in low-alloy steels to form methane (CH_4) bubbles (ref. 32). This type of hydrogen embrittlement is commonly represented by Nelson diagrams which describe the safe operating conditions for steels in hydrogen environments. Another example is the reaction of hydrogen with oxygen in copper to form steam (H_2O) resulting in blistering and a porous metal component.

Internal reversible hydrogen embrittlement. - Internal reversible hydrogen embrittlement has also been termed slow strain rate embrittlement and delayed failure. This is the classical type of hydrogen embrittlement that has been studied quite extensively. Hydrogen is absorbed from any source and is diffusible within the metal lattice. To be fully reversible, embrittlement must occur without the hydrogen undergoing any type of chemical reaction after it has been absorbed within the lattice. Widespread attention has been focused on the embrittlement problem resulting from electroplating - particularly of cadmium on high-strength steel components. Other sources of hydrogen are processing treatments such as melting and pickling. More recently, the embrittling effects of many stress-corrosion processes have been attributed to corrosion-produced hydrogen.

Internal reversible hydrogen embrittlement can occur after a very small average concentration of hydrogen has been absorbed from the environment. However, local concentrations of hydrogen are substantially greater than average bulk values. For steels, embrittlement is usually most severe at room temperature during either delayed failure (static fatigue) or slow strain rate tension testing. This time-dependent nature (incubation period) of embrittlement suggests that diffusion of hydrogen within the lattice controls this type of embrittlement. Cracks initiate internally, usually below the root of a notch at the region of maximum triaxiality. Embrittlement in steel is reversible (ductility can be restored) by relieving the applied stress and aging at low temperatures provided microscopic cracks have not yet been initiated. Internal reversible hydrogen embrittlement has also been observed in a wide variety of other materials including nickel-base alloys and austenitic stainless steels provided they are severely charged with hydrogen (refs. 33 and 34). Figure 2 illustrates that such embrittlement can significantly reduce room temperature ductility of such materials.

Hydrogen environment embrittlement. - Hydrogen environment embrittlement was recognized as a serious problem in the mid 1960's when the National Aeronautics and Space Administration (NASA) and its contractors (refs. 35 and 36) experienced failures of ground based hydrogen storage tanks (see table II). These tanks were rated for hydrogen at pressures of 35 to 70 MN/m² (5000 to 10 000 psi). Because of these failures and the anticipated use of hydrogen in advanced rocket and gas-turbine engines and auxiliary power units, NASA has initiated both in-house and contractual research dealing with this problem. The thrust of the contractual effort generally has been to define the relative susceptibility of structural alloys to hydrogen environment embrittlement. A substantial amount of research has been concerned with the mechanism of the embrittlement process. There is marked disagreement as to whether hydrogen environment embrittlement is a form of internal reversible hydrogen embrittlement or is truly a distinct type of embrittlement.

Hydrogen environment embrittlement has been observed over a wide range of gas pressures, temperatures, and in a variety of mechanical tests (refs. 37 to 42), see table III. Embrittlement appears to be most severe near room temperature. Gas purity and test strain rate can play significant roles in determining the degree of embrittlement. The transfer step of surface adsorption has been shown to be the overall rate-controlling step during hydrogen environment embrittlement (refs. 43 and 44). However, if adsorption is bypassed, the rate-controlling step for hydrogen environment embrittlement is either absorption or subsequent lattice diffusion. Quantitative analyses indicate substantial increases in the hydrogen content of embrittled alloys and tend to support the necessity for lattice diffusion to occur since it is unlikely that such large quantities of hydrogen can be absorbed within the first atomic layer below the surface. Another important characteristic of hydrogen environment embrittlement that has not been conclusively resolved is the location of crack initiation - whether it starts at the surface or internally. These characteristics are compared in table III with those observed for internal reversible hydrogen embrittlement and for hydrogen reaction embrittlement.

Hydrogen environment embrittlement has also been observed in a wide variety of materials. The high strength structural alloys such as steels and nickel-base alloys are particularly susceptible. Metals and alloys subject to all types of hydrogen embrittlement are listed in table IV. Those affected by hydrogen environment embrittlement and internal reversible hydrogen embrittlement are listed in the approximate order of decreasing susceptibility at room temperature. The metals affected by hydrogen reaction embrittlement are also listed in table IV, and the types of reactions are called out.

Embrittlement Problems During Hydrogen Production

Hydrogen production and coal gasification processes, as well as advanced energy conversion systems, involve hydrogen as a product of one of the reaction steps or as a heat transfer medium. In these processes containment of hydrogen at various temperatures up to 2000^o C and pressures up to 7 MN/m² (1000 psi) is an important design consideration. The goals of advanced energy conversion and generation systems are to: (1) increase service temperatures which equates to increased thermal efficiency, (2) increase reliability which equates to increased availability of supply, (3) reduce failure which equates to reduced personnel hazard, and (4) reduce capital requirements. Such goals bring into focus a myriad of materials problems associated with hydrogen containment.

Fortunately, the requirements for hydrogen containment at high temperatures and pressures have existed for a number of years in the ammonia and petroleum hydrorefining industries. Much technology has been developed which may be applicable at the least partially to the anticipated requirements for hydrogen production. However, there are strong indications that the Nelson curves (see fig. 1) used to design against elevated temperature hydrogen attack are inadequate. The Nelson curves are constructed from data obtained from plant failure experience and satisfactory operating experience, accumulated over many years. These curves delineate the safe and unsafe hydrogen pressure-temperature regimes for carbon and alloy steel in a purely empirical way. Each successive revision of these curves seems to widen the operating limits under which hydrogen attack is observed by lowering the allowable temperature or pressure for safe usage of a given steel.

It is both a strength and a weakness of the design approach using Nelson curves that it is based solely upon accumulated practical experience. The hydrogen gas environments are those used in the petrochemical industry and are far from pure. No attempt has been made previously to define the gas composition of the environments and thus these empirical observations may well reflect effects of gases other than hydrogen.

The objective of a recently initiated, joint NASA-Ames and Electric Power Research Institute program is to establish the technology necessary to select steels to design economical and reliable pressure vessels for use in the aggressive, high temperature, hydrogen-rich environments of coal gasifiers. This joint effort of NASA and EPRI consists of a four-component program having as separate objectives:

- (1) To establish the current state-of-the-art of high temperature pressure vessel technology.

(2) To expand our current understanding of the responsible kinetic and mechanistic aspects of the problem.

(3) To develop by analytical means the life prediction and failure criteria for gasifier pressure vessels.

(4) To develop improved low-cost steel alloys for gasifier service.

EPRI will use its funds and unique connection with the operating power companies to accomplish objectives 1, 3, and 4 above. NASA will apply its background and talents with similar environment/material interactions to accomplish objective 2 through a combined in-house and contractual program. Specifically, studies will be conducted on carbon and low alloy steels in contact with pure hydrogen and hydrogen-rich environments containing mixtures of other relevant constituents. The kinetic processes involved in the transport of hydrogen from the environment through the steel and its interaction with the steel will be investigated as a function of temperature, pressure, and applied stress. The effect of other gaseous species, modifications of the alloy composition and microstructure of the steel, and chemical modifications of the environment will be studied. The mechanism of attack will be defined by changes in the mechanical properties of steels both at room temperature after exposure at elevated temperatures, as well as during exposure to hydrogen-rich gaseous environment at elevated temperatures. The results of these kinetic and mechanistic studies will be correlated in an effort to understand and predict the rate and severity of material property degradation by hydrogen-rich gaseous environments. The results of this program should be of significant benefit not only for coal gasification processes but also for hydrogen production processes.

Hydrogen Embrittlement During Transmission/Storage/Utilization

Hydrogen is envisioned as being transported in gaseous or liquid form and as being stored in either of these two forms or possibly as a solid hydride phase. Presently, we are capable of designing transport and storage facilities for hydrogen or hydrogen-rich gases which are reasonably free from environmental degradation over their lifetimes. However, these designs have important limitations and involve either relatively expensive alloy systems containing alloy elements such as chromium and nickel which may eventually be considered scarce, or involve the inefficient use of large quantities of less expensive materials. The cost of acceptably safe systems may be too high unless we establish criteria to make the most effective use of materials consistent with reasonable levels of safety.

Liquid hydrogen. - The transport and storage of hydrogen in the liquid phase presents unique problems. At cryogenic temperatures encountered in liquid hydrogen systems, most reaction processes, including the dissociation of molecular hydrogen, are very slow and the movement of hydrogen from the environment into the metal becomes very difficult. Most of the material problems encountered by NASA in its Apollo and Skylab programs were not directly associated with the hydrogen used in their propellant systems. For example, corrosion of stainless steel nuts, piping, and bellows occurred because of improper material choices, inadequate galvanic corrosion protection, or insufficient protective coatings. Other problems can be encountered, however, if the system is subjected to thermal cycling where hydrogen is allowed to enter the metal at high temperatures. Under such conditions, a second phase, either gaseous or solid (hydride), may form and result in hydrogen reaction embrittlement which could severely degrade the reliability of the transport or storage system. Stable austenitic stainless steels or aluminum alloys should find continued application in liquid hydrogen transport or storage systems.

One uncertainty remains in using an austenitic stainless steel for long-term service at low temperatures. There is a tendency for martensite to form to a greater or lesser degree depending on steel composition. Some martensite will form on cooling in 304L, but not in 310 or 316. Isothermal martensite formation over long periods of time has not been studied in these steels to the best of our knowledge. Rate of formation data and the tolerance level for martensite should be determined before the best choice of materials can be made.

Hydride storage. - The materials problems associated with hydrogen storage in the form of hydrides differ greatly from those encountered in gaseous or liquid hydrogen storage systems. Here, high temperatures, high pressures, and thermal cycling are encountered as part of the operating design (refs. 45 and 46).

As an example, consider the reservoir built by Brookhaven National Laboratory for using iron titanium hydride ($\text{FeTiH}_{1.6}$) as a medium for storing hydrogen generated by off-peak electrical energy. The pressure vessel was made from a section of 316 stainless steel pipe, 30 cm in diameter and 0.6 cm wall thickness. The vessel must contain hydrogen at 3 NM/m^2 (500 psi) pressure at ambient temperature. The highest temperature the vessel reaches in the hydride-dehydride cycle is approximately 60°C . This temperature probably is not high enough to cause hydrogen reaction embrittlement (blistering from methane or hydrogen gas).

However, potential problems may occur when hydride compounds which dissociate at a higher temperature are substituted for $\text{FeTiH}_{1.6}$. For example, if TiH_2 or MgH_2 were used, the maximum operating temperatures would be approximately 600° and 400°C , respectively. At these temperatures, hydrogen embrittlement

could be a problem with either a stainless or a low alloy steel.

Caseous hydrogen. - Most present gaseous hydrogen transmission systems in the aerospace and petrochemical industries involve either relatively short pipeline systems or the use of mobile tanks. Most local hydrogen transmission systems operate at 3 MN/m^2 (450 psi) or less with the exception of some systems in the petrochemical industry operating at 7 MN/m^2 (1000 psi). They are constructed of relatively small diameter pipe of some austenitic stainless steel, and are not of sufficient length to require in-line compressors.

In addition to the relatively short pipeline systems mentioned above for "captive" hydrogen, there are at least five pipelines distributing "merchant" hydrogen in the world. A summary of all available data (refs. 1, 4, 47, and private communication by authors of this report) for hydrogen pipelines is listed in table V. All of these pipelines, except the one at Los Alamos (ref. 45), have apparently been operating without any problems attributable to hydrogen embrittlement. However, the Los Alamos pipeline cracked, leaked, and was finally abandoned. Failure was attributed to poor galvanic corrosion protection, poor weld quality, and use of a steel susceptible to hydrogen embrittlement. None of these pipelines have any in-line compressor stations.

A limited amount of laboratory data (refs. 48 and 49) also suggests that hydrogen environment embrittlement may be a potential problem with typical pipeline and pressure vessel steels (see figs. 3 and 4). These data indicate that: (1) low strength steels are embrittled, (2) weldments are particularly susceptible, and (3) embrittlement occurs at hydrogen pressures as low as 0.3 to 7 MN/m^2 (50 to 1000 psi). These data are particularly significant since it is occasionally assumed that hydrogen embrittlement is a problem only when using high strength steels in high pressure hydrogen.

CONCLUDING REMARKS

The primary consideration in a hydrogen transmission and storage system is one of cost. Economic considerations include operating costs, capital investment, and available resources. Additionally, to some extent, there is also a trade-off with respect to safety. One point of view is that public acceptance of current rates of failures in public transportation and gas pipeline systems can be extrapolated to extended hydrogen usage and thus no new, stringent requirements would be necessary. The second, and probably more likely point of view, is that the public will demand low failure rates for hydrogen systems, much the same as those required presently for nuclear reactor systems. Such a requirement for a low failure rate means that it is simply inappropriate to assume that much of the current experience can be readily extended to the new engineering circumstances

encountered in hydrogen systems. If the latter position prevails, much research will be required to prove any new system.

Some consideration has been given to the possibility of using the present natural gas distribution system as an extended distribution system for gaseous hydrogen. Major differences exist between methane, the primary gas constituent of natural gas, and hydrogen which appear to make this economically unfeasible. The heat of combustion of hydrogen is 325 Btu/cubic foot compared with 1013 Btu/cubic foot for methane. Additionally, the compressibility of hydrogen at 23° C and 10 MN/m² (1450 psi) is 1.06 compared with 0.855 for methane. The energy throughput for hydrogen is about one-fourth that for natural gas. Therefore, the economics of the situation demands the operation of these pipelines at their maximum operating pressures.

The present natural gas distribution system within the USA involves more than 1 500 000 km (900 000 miles) of pipeline of which about 400 000 km (250 000 miles) are mains. These pipelines are made primarily of low carbon steel (e. g., 1015 or 1020), are of varying age, manufacture, diameter, thickness, and fabrication practice, and operate at pressures near 7 MN/m² (1000 psi). The stress level in these pipelines is set by a design code at 72 percent of the pipe steel tensile yield strength. To operate such a pipeline at 72 percent of its yield strength with hydrogen would, in our opinion, be unthinkable because of the safety hazard associated with hydrogen compared with methane. The flammability limit in air for hydrogen ranges from about 4 to 92 percent with flamespeeds through this range from 0.3 m/sec to a maximum of 3 m/sec. On the other hand flammability limits for methane range from about 8 to 15 percent with a maximum flame-speed of 0.3 m/sec. It appears most unwise to contemplate pumping hydrogen through our natural gas system without a full-scale field validation.

Current methods of minimizing hydrogen environment embrittlement of transmission and storage systems include the correct selection of materials, ensurance of sound welds, design to minimize stress concentrations, the use of gaseous inhibitors, and the use of coatings. The variable of selecting expensive, highly alloyed materials for new, extended gaseous hydrogen pipelines appears economically unfeasible. Economics of transport suggest pipelines of up to 1.2 meters in inside diameter operating at pressures approaching 14 MN/m² (2000 psi). If a steel could be developed or be made safe from hydrogen environment embrittlement to 72 percent of its yield strength, a 450 MN/m² (65 ksi) steel pipeline would require a wall thickness of approximately 3 cm. The amount of material required for such a pipeline becomes very large and thus inexpensive materials must be used. Designers will no longer have the option of using an austenitic stainless steel rather than a ferritic steel for hydrogen service.

RECOMMENDED RESEARCH AND DEVELOPMENT PROGRAMS

It is suggested that a research program is needed to better understand how hydrogen gets from the environment to a location in the metal where the process of property degradation occurs. The eventual goal should be to control these transport processes. Emphasis should be placed on practical environments expected to be encountered in real systems. The roles of specific inhibitors on the movement of hydrogen into metals should be explored in detail. Inhibitors can take the form of additives to the gaseous environment or to the metal itself, or consist of protective coatings. If any one of the reaction steps involved in the transport of hydrogen from the environment to the metal can be hindered or prevented, less expensive materials could then be used efficiently and safely for hydrogen systems.

Research should also be undertaken to study the influence of cyclic loading on the environmental degradation of materials used not only for pipelines but also for in-line compressor pumps, valves, etc. In-line compressors will be a necessity in large hydrogen transport systems.

Specific research and development programs suggested are:

1. Evaluation of welded pipeline steel under simulated service conditions.
2. Evaluation of candidate compressor alloys under simulated service conditions.
3. Compatibility of materials in corrosive environments associated with most promising hydrogen production processes (as soon as production processes are reasonably well defined).
4. Improved welding and nondestructive inspection technologies.
5. Determine feasibility of composite pipelines (thin metal liner with fiber-glass overwrap).

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TABLE I. - POTENTIAL MATERIALS PROBLEMS IN HYDROGEN

ENERGY SYSTEMS

Production

<u>Feedstock</u>	<u>Process heat source</u>	<u>Production technique</u>	<u>Materials problems</u>
Water	Nuclear	Thermochemical split	Hydrogen embrittlement
Gas	Solar	Electrolysis	Tritium permeation
Oil	Geothermal	Coal gasification	Corrosion
Coal	Coal	Direct water split	Acids
		Steam reforming	Halides
		Partial oxidation	Brine
			Liquid metals
			Heat transfer fluids and salts
			Oxidation
			Carburization
			Decarburization
			Sulfidation
			Nitridation
			Erosion
			Coal slurries
			Heat transfer slurries
<u>Transmission/Storage</u>	(Gas, liquid, or hydride)		Hydrogen embrittlement
<u>Utilization</u>	(Gas, liquid, or hydride)		Hydrogen embrittlement

TABLE II. - HYDROGEN STORAGE SYSTEM FAILURES (REFS. 35 AND 36)

Year	Location	Number of failures	Pressure		Material	Type of failure
			MN/m ²	psi		
Ground storage tanks						
1964-65	Aerojet	5	35	5 000	1146a steel	Nozzle leaks at welds
1965	Aerojet	3	35	5 000	A517-F	Cracks up to 1.3 m
1966	NASA	3	20	3 000	A517-F	Inner shell cracked and leaked
1967	Aerojet	1	25	3 600	A517-F	Cracks up to 1.5 m
----	Sud Aviation	1	120	17 000	Maraging	Explosion
Bourdon tubes in pressure gages						
1964-67	NASA	---	---	-----	403 and 431 stainless steels, Inconel X	Rupture, fire, and injury

TABLE III. - CHARACTERISTICS OF TYPES OF HYDROGEN EMBRITTLEMENT (REF. 31)

Characteristic	Type of embrittlement			Hydrogen reaction embrittlement
	Hydrogen environment embrittlement	Internal reversible hydrogen embrittlement	Processing } (H) Electrolysis } Corrosion }	
Usual source of hydrogen	Gaseous (H ₂)			Gaseous or atomic hydrogen from any source
Typical conditions	10 ⁻⁶ to 10 ⁻⁸ N/m ² gas pressure Most severe near room temperature Observed from -100° to 700° C Gas purity is important Strain rate is important	0.1 to 10 ppm average H content Most severe near room temperature Observed from -100° to 100° C Strain rate is important		Heat treatment or service in hydrogen, usually at elevated temperatures
Test methods	Notched tensile Unnotched tensile Creep rupture Fatigue (low, high cycle) Fracture toughness Disk pressure test	Notched delayed failure Slow strain rate tensile Bend tests C-rings Torqued bolts		Can be observed visually or metallographically
Crack initiation	Surface or internal initiation ^a	Internal crack initiation Incubation (reversible) Slow, discontinuous growth Fast fracture		Usually internal initiation from bubbles or flakes
Rate-controlling step	Adsorption is transfer step Absorption or lattice diffusion ^a is embrittling step	Lattice diffusion to internal stress raisers		Chemical reaction to form hydrides or gas bubbles

^aUnresolved.

TABLE IV. - METALS AND ALLOYS EMBRITTLED BY HYDROGEN (REF. 31)

hydrogen environment embrittlement ^a	Internal reversible hydrogen embrittlement ^a	Hydrogen reaction embrittlement
<p>High strength steels 18Ni Maraging 410, 440C, 430F, 403, 431 H-11, 4140, 1042 (Q&F) Fe-9Ni-4Co, 17-7PH</p> <p>Nickel and nickel alloys Electroformed Ni Nickel 200, 270, 301 Inconel 625, 700, 706, 718, X Rene 41, Hastelloy X Udimet 700, Waspaloy MAR M-200DS, IN 100</p> <p>Low strength steels Armco iron, CK22, CK45, 1020 1042 Nor., HY-80, HY-100 A-302, A-515, A-517, A-533B 1146a, HY-130, SA105</p> <p>Titanium alloys Ti-6Al-4V, Ti-5Al-2.5Sn</p> <p>Molybdenum-TZM</p> <p>Cobalt alloys HS-188, L-605, S-816</p> <p>Metastable stainless steels 304L, 305, 310, 309S</p> <p>K-Monel</p> <p>Be-Cu Alloy 25</p> <p>Pure titanium</p> <p>Stable stainless steels 316, 321, 347, A-286 Armco 21-6-9, 22-13-5</p> <p>Copper alloys, OFHC Cu TD-Ni, TD-NiCr</p> <p>Magnesium alloy HM21A</p> <p>Aluminum alloys 1100, 2219, 6061, 7039, 7075</p>	<p>High strength steels 4340, 4140, H-11 17-7PH, A1885 18Ni Maraging E8740, 17-7PH</p> <p>Exp. Fe-Ni-Cr alloys</p> <p>Exp. Fe-Cu alloys Ti, Zr, V, Nb, Ta Cr, Mo, W, Co, Ni Pt, Cu, Au, Al, Mg and/or some of their alloys</p> <p>Metastable stainless steels 304L, 310</p> <p>K-Monel</p> <p>High strength nickel alloys Inconel 718 Rene 41 Waspaloy Hastelloy X</p> <p>Stable austenitic steels 316, A-286, U-212, 21-6-9</p>	<p>Hydrides (MH_x) H reacts with matrix Ti, Zr, Hf, V, Nb, Ta Mn, Ni, Pd, U, Pu, Th Rare earths Alkalies Alkaline earths</p> <p>H reacts with element in matrix MgZr, MgTh alloys</p> <p>High pressure gas bubbles H reacts with itself (H₂) Steels, OFHC Cu Ni, Al, Mg, Be</p> <p>H reacts with foreign element in matrix CH₄ in low alloy steels, Ni alloys H₂O in welded steels, Cu, Ni, Ag NH₃ in molybdenum</p>

^aListed in approximate order of decreasing susceptibility at room temperature.

TABLE V. - HYDROGEN PIPELINE EXPERIENCE

Location	Pipeline steel	Age, yr	Diameter, cm	Length, km	Hydrogen			Comments
					Purity	Pressure		
						MN/m ²	psi	
Air Products - Texas	Converted natural gas line	6	10	8	99.5%	6	800	No problems
Air Products - Texas	New-schedule 40 steel	3	20	19	99.5%	1.4	200	No problems
Germany	Seamless 1015 steel	Up to 35	15 - 30	210	Dirty ^a	1.8	260	No problems
NASA-KSC - Florida	316 Stainless steel	10	5	1.6	Ultrapur ^b	42	6000	No problems
Linde	-----	-----	-----	1.6 - 3	-----	-----	-----	-----
South Africa	-----	-----	-----	80	-----	-----	-----	-----
Los Alamos	5Cr-Mo steel	8	3	6	Ultrapur ^b	14	2000	Leaked in 3 yr, cracked in 4 yr, abandoned

^a Purity unknown. 12 materials transported interchangeably through pig line.

^b Liquid boiloff.

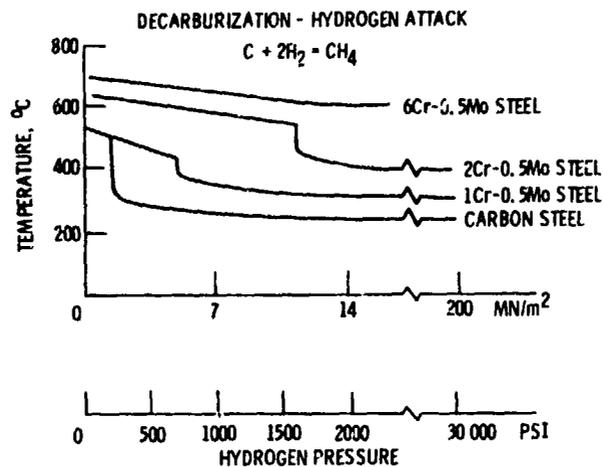


Figure 1. - Nelson diagram describing the safe operating limits for steels in hydrogen and hydrogen-containing environments (32).

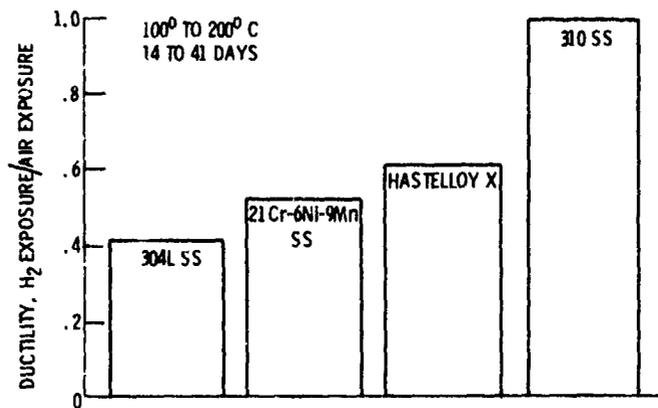


Figure 2. - Effect of exposure in 70 MN/m² (10 000 PSI) hydrogen on the room temperature ductility of austenitic stainless steels and a nickel-base superalloy, hastelloy X (33).

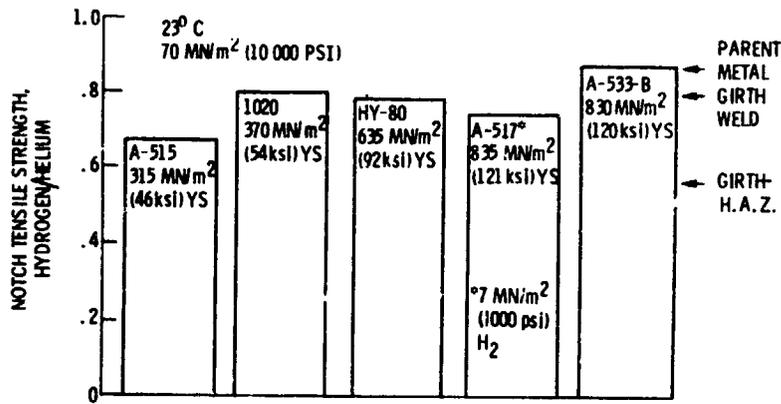


Figure 3. - Effect of hydrogen (99.999%) on notch tensile strength of pipeline and pressure vessel steels (48).

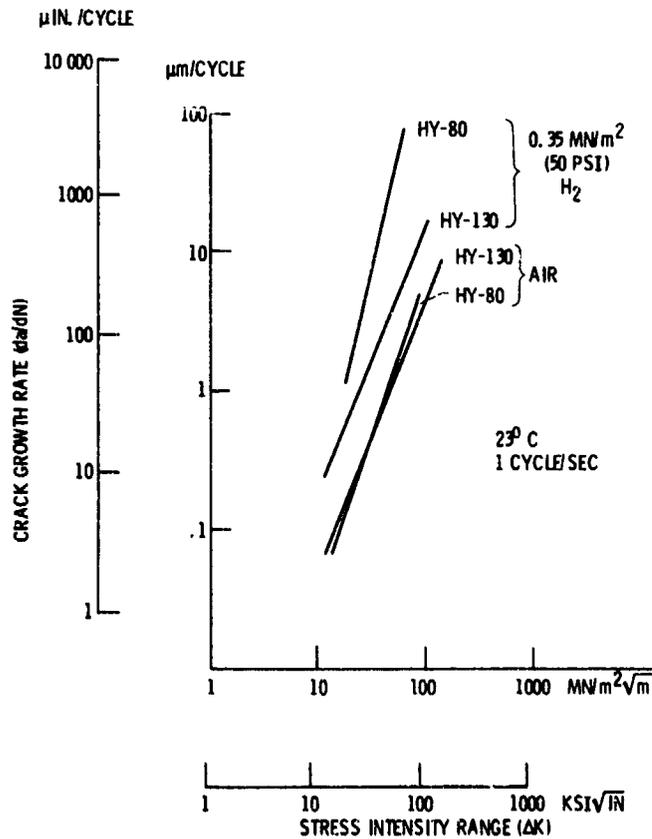


Figure 4. - Cyclic crack growth of pressure vessel steels in hydrogen (99.9%) and in air (49).